Environmental testing

Positive chemical ionization using the Thermo Scientific ISQ 7610 single quadrupole GC-MS system

Authors

Amit Gujar[1], Kenneth M. Free[1],
Tim Anderson[1], and Adam Ladak[2]

[1]Thermo Fisher Scientific, USA
[2]Thermo Fisher Scientific, UK

Keywords

Chemical ionization (CI), positive chemical ionization (PCI), electron ionization (EI), GC-MS, ISQ 7610, NeverVent technology, TRACE 1610
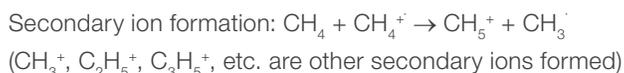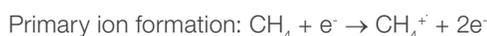
Introduction

Gas chromatography-mass spectrometry (GC-MS) is a popular analytical technique used for unknown compound identification and quantitation. The technique finds utility in a variety of markets, such as environmental, food, clinical/toxicological, and petrochemical analysis. Electron ionization (EI) is the most common ionization technique utilized in GC-MS instruments. One of the primary advantages of EI is that the fragmentation pattern of a molecule using 70 eV electron energy is consistent, and this electron energy is used among various instrument manufacturers. The commercially available spectral libraries, such as those from NIST and Wiley, contain spectra generated at 70 eV, which can be used for identifying known unknowns. However, one of the disadvantages of EI is that some compounds show little or no molecular ion, and therefore identification of unknown compounds is difficult to confirm. This is especially true for compounds that are not in available libraries. In this case, a "softer" ionization technique is useful for preserving the molecular ion. Chemical ionization (CI) is one such soft ionization technique. There are two primary modes of CI, positive ion chemical ionization (PICI or PCI) and negative ion chemical ionization (NICI or NCI). It is more appropriate to refer to NCI as electron capture negative ionization (ECNI) since negative ions are mainly formed by low-energy electron capture as opposed to ion-molecule reactions prevalent in PCI.

PCI is an ion-molecule reaction as opposed to an electron-molecule reaction that occurs in EI. The two essential requirements for PCI are a closed ion volume, which helps maintain relatively high pressures required for PCI, and the presence of an appropriate reagent gas that undergoes ionization under an electron beam (similar to what happens in EI). To perform chemical ionization effectively, a dedicated ion volume should be utilized that has smaller diameter openings with low conductance.

One of the major advantages of Thermo Scientific™ NeverVent™ technology on the Thermo Scientific™ ISQ™ 7610 GC-MS system is the ability to change between dedicated EI and CI ionization sources without venting the system. This means an operator can change ionization modes within a few minutes, which allows samples to be analyzed rapidly in ideal ionization conditions.

The reagent gases that are commonly used for chemical ionization include methane, ammonia, and iso-butane. The reagent gas ions react with other reagent gas and analyte molecules to undergo ion-molecule reactions that serve as the basis of PCI. When methane is used as a reagent gas the reactions include:

Primary ion formation: $CH_4 + e^- \rightarrow CH_4^{+\cdot} + 2e^-$

Secondary ion formation: $CH_4 + CH_4^{+\cdot} \rightarrow CH_5^+ + CH_3^\cdot$
(CH_3^+, $C_2H_5^+$, $C_3H_5^+$, etc. are other secondary ions formed)

These secondary ions can be clearly seen from the mass spectrum of methane reagent gas in PCI mode in Figure 1. The major ions m/z 29, m/z 41, and m/z 17 are $C_2H_5^+$, $C_3H_5^+$, and CH_5^+, respectively.

The analyte molecules react with the primary and secondary methane reagent gas ions to form M^+, $[M+H]^+$, $[M-H]^+$, $[M+C_2H_5]^+$, and $[M+C_3H_5]^+$ ions.

$M + CH_5^+$	$\rightarrow$	$CH_4 + [M+H]^+$ (Protonation)
$AH + CH_3^+$	$\rightarrow$	$CH_4 + A^+$ (Hydride abstraction)
$M + C_2H_5^+$	$\rightarrow$	$[M+C_2H_5]^+$ (Adduct formation)
$M + CH_4^{+\cdot}$	$\rightarrow$	$CH_4 + M^{+\cdot}$ (Charge exchange)

The presence of $[M+1]^+$, $[M+29]^+$, and $[M+41]^+$ ions with methane-PCI are good confirmation for the molecular ion.[1,2,3]
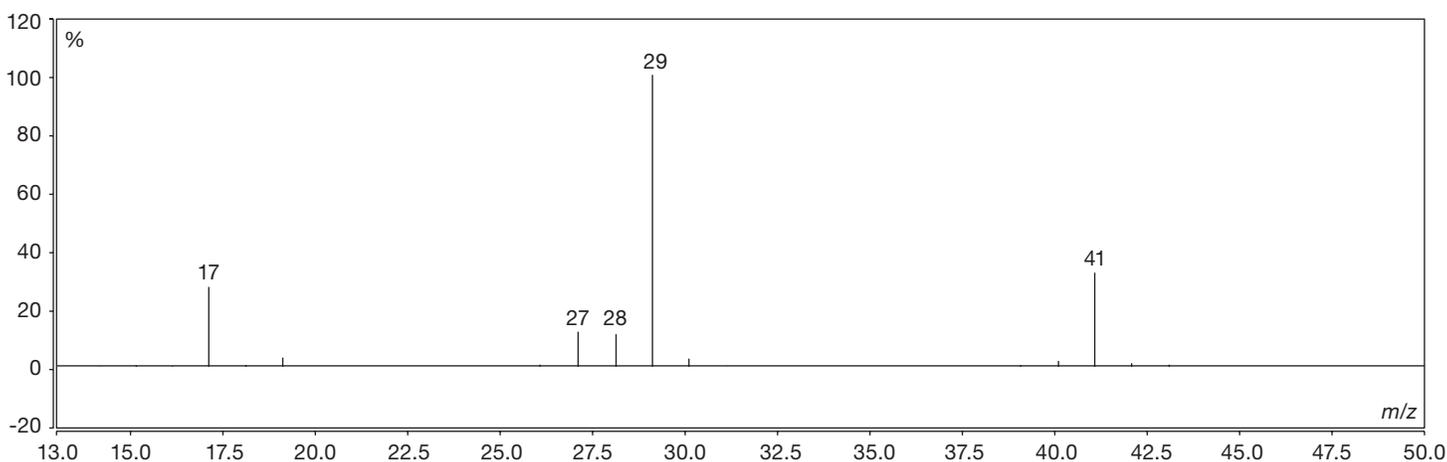
This technical note will focus on the analysis of compounds using PCI with the ISQ 7610 GC-MS. Examples of semi-volatile compounds (SVOC) of various analyte types and their behavior in PCI mode will be demonstrated and compared to the EI spectra. The effect of varying the ion source temperature on PCI is also demonstrated.

Experimental

The PCI experiments were conducted on a Thermo Scientific™ TRACE™ 1610 GC and Thermo Scientific™ AI/AS 1610 autosampler coupled with an ISQ 7610 MS system with NeverVent technology. The analytes used for this study were the Restek 8270 MegaMix™ (Catalog # 31850), which contains 76 SVOC compounds with varying functional groups. A 10 ppm mixture was prepared by diluting the standards with dichloromethane (DCM). Analysis was done in both EI and PCI modes. The experimental conditions of these experiments are given in Table 1.

Table 1. Instrument method conditions for the PCI experiments

AS 1610 Autosampler	
Syringe	10 µL, 25 gauge, 50 mm length, cone tip (**P/N 36500525**)
Injection volume	1 µL
Pre-injection solvent and cycles	None
Sample rinses	3
Post-injection solvent and cycles	None

Figure 1. Mass spectrum of methane reagent gas in PCI mode

TRACE 1610 GC system	
Column	Thermo Scientific™ TraceGOLD™ TG-5MS, 30 m × 0.25 mm × 1.0 µm
Liner	Splitless Liner single taper with wool, 4 mm i.d., 78.5 mm length (P/N 453A0924)
SSL mode	Split
Inlet temperature	300 ˚C
Split flow	15 mL/min (split ratio = 8)
Septum purge flow	Constant flow of 5.0 mL/min
Carrier flow	Constant He flow of 1.8 mL/min
Oven program	60 ˚C (1.0 min), 10 ˚C/min to 265 ˚C (1 min), 2 ˚C/min to 315 ˚C (2 min)
ISQ 7610 GC-MS system	
MS transfer line temperature	300 ˚C
Ion source temperature	Varied from 150 to 320 ˚C
Source type	Thermo Scientific™ ExtractaBrite™ with CI ion volume
Ionization mode, electron energy	PCI, 70 eV
Emission current	50 µA
Scan range	45–500 Da
Dwell time	0.2 s
Detector gain	3E+05
Tuning used	AutoTune_PCI

Experiments were initially conducted in EI mode to ascertain the identity of compounds using the NIST library.

Note on PCI tuning: The tuning for PCI mode is done using FC43 (PFTBA) as the calibration gas. This is the same as that for EI tuning but the AutoTune routine performs the mass calibration and resolution tuning on m/z 219, m/z 414, and m/z 652. Figure 2 shows the FC43 calibration mass spectrum in PCI mode.

Results and discussion
EI and PCI spectral comparison
Figure 3 shows the total ion chromatogram (TIC) comparison of the 8270 SVOC mix under the same GC conditions. All expected analyte peaks were observed in both EI and PCI modes.

Mass spectral comparisons for each of these analytes show a distinct difference. For example, Figure 4 shows mass spectrum comparison of the peak for pyridine (molecular weight - 79 Da) in EI and PCI modes. The EI spectrum shows the presence of the molecular ion, M$^+$ (m/z 79), and the expected fragmentation pattern matches that of the NIST library (SI match score of 934). The PCI mass spectrum shows the protonated molecule, M+1$^+$ (m/z 80) and the presence of adduct ions, M+29$^+$ (m/z 108) and M+41$^+$ (m/z 120).

Figure 5 shows the comparison of EI and PCI mass spectra for nitrobenzene where protonation is the major reaction mechanism for PCI with little to no adduct formation occurring. One also observes less fragmentation of the molecular ion in the PCI mode.
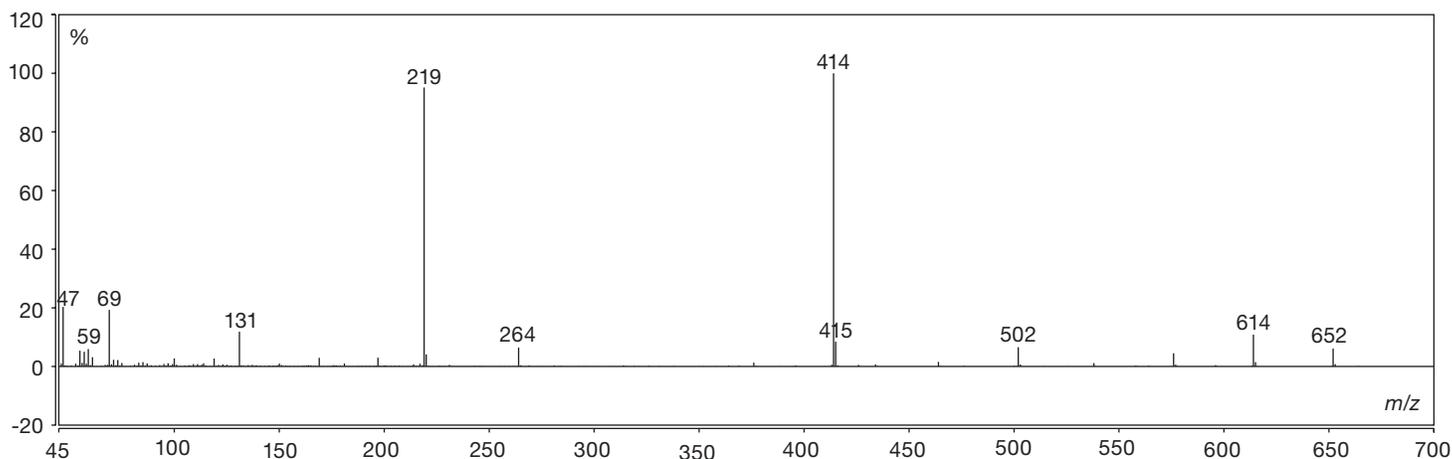

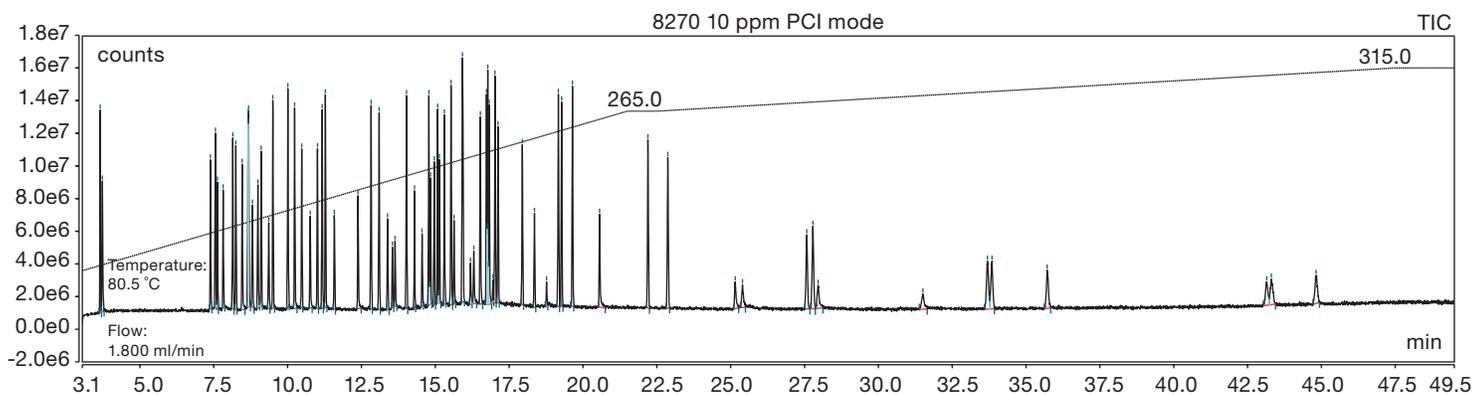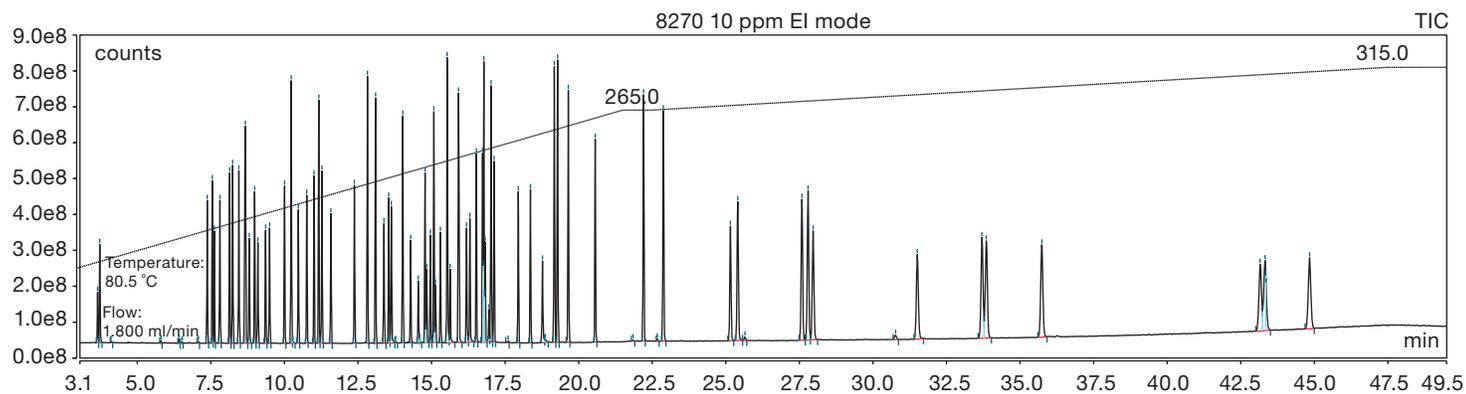Figure 2. Mass spectrum of FC43 cal gas in PCI mode

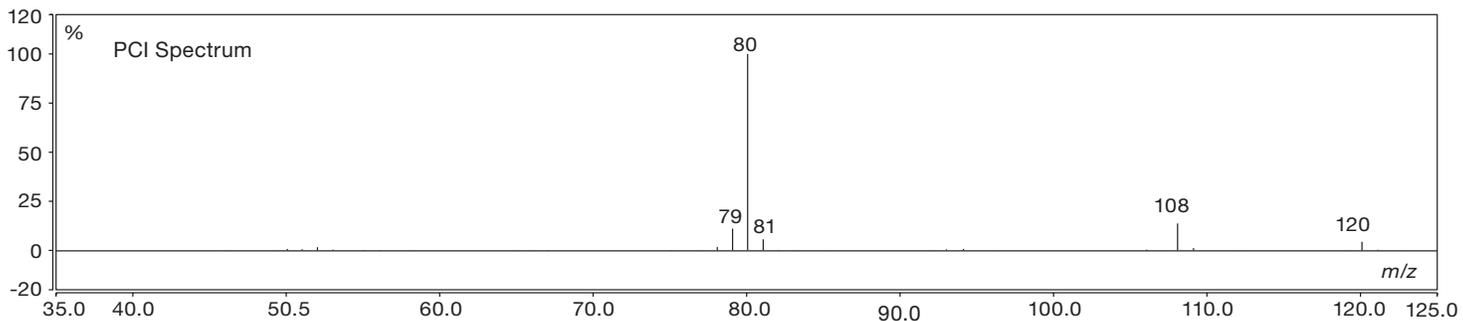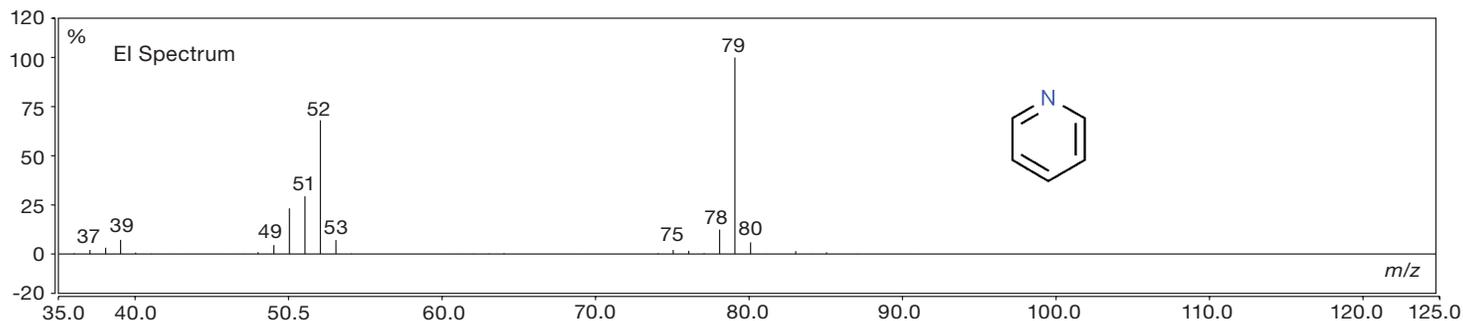Figure 3. Comparisons of TICs of the 8270 SVOC mix in EI and PCI modes

Figure 4. Comparison of the mass spectrum for pyridine in EI and PCI modes
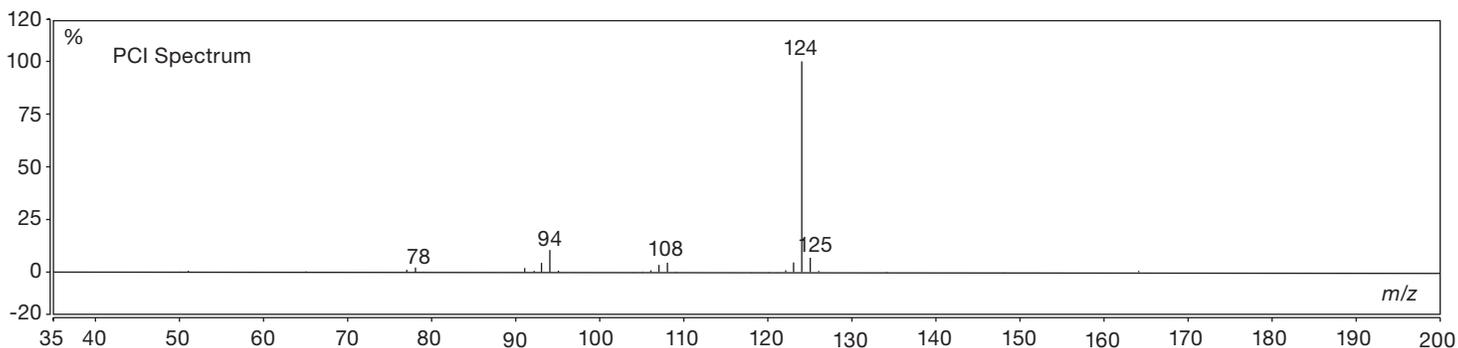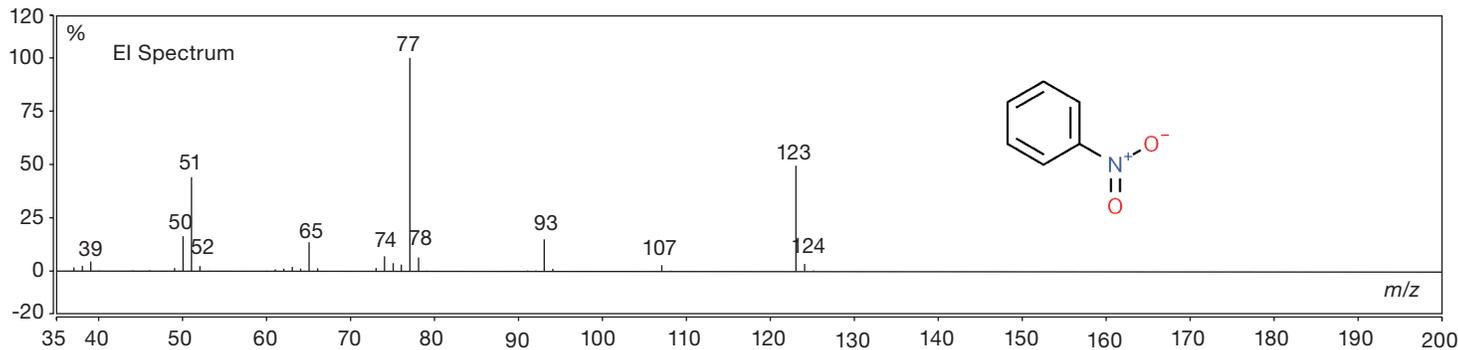
Figure 5. Comparison of the mass spectrum for nitrobenzene in EI and PCI modes

Figure 6 shows a comparison for EI and PCI mass spectra for hexachlorocyclopentadiene, and neither protonation nor adduct formation is observed. In this case, a simple charge exchange between the reagent gas and the analyte molecule occurs and both EI and PCI mass spectra look similar. The NIST library hits in both modes give hexachlorocyclopentadiene as the first hit but with the PCI mode having a much lower SI match factor.

Figure 7 shows an example of diethyl phthalate (molecular weight - 222 Da) where there is almost complete fragmentation of the molecular ion in the EI mode. Even though the NIST library shows diethyl phthalate as the first hit, it is plausible for the user to doubt this because of the lack of observable molecular ion. In this case, PCI can be used as a confirmation technique. One observes the typical M+1[+], M+29[+], and M+41[+] pattern associated with methane-PCI.
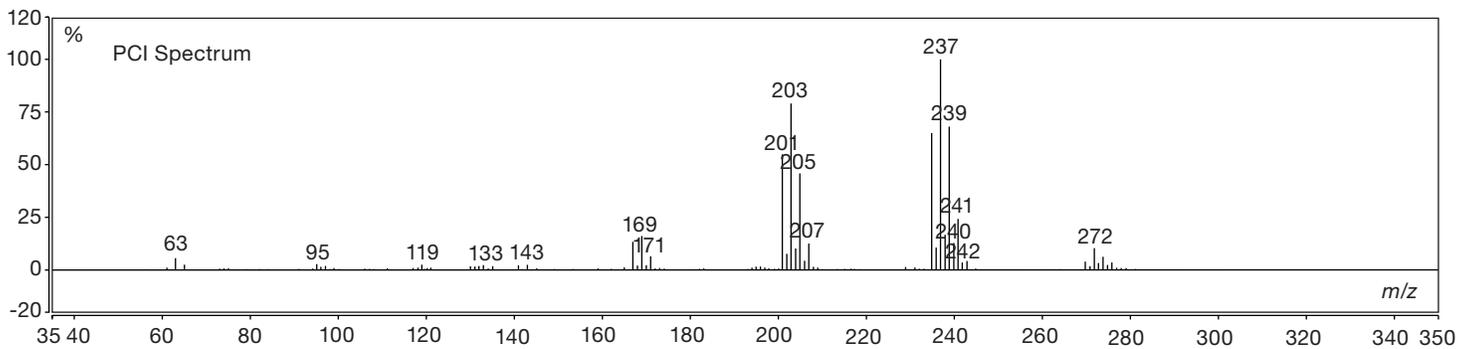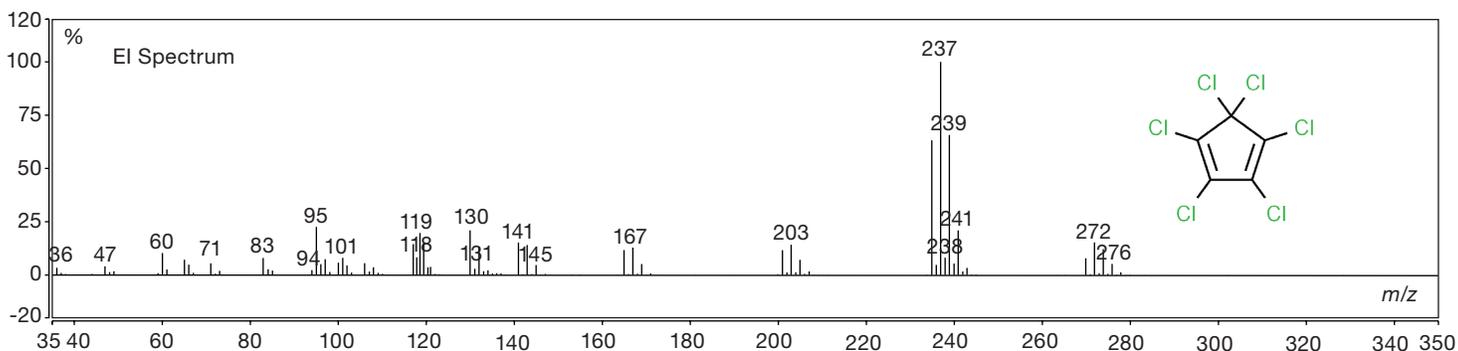

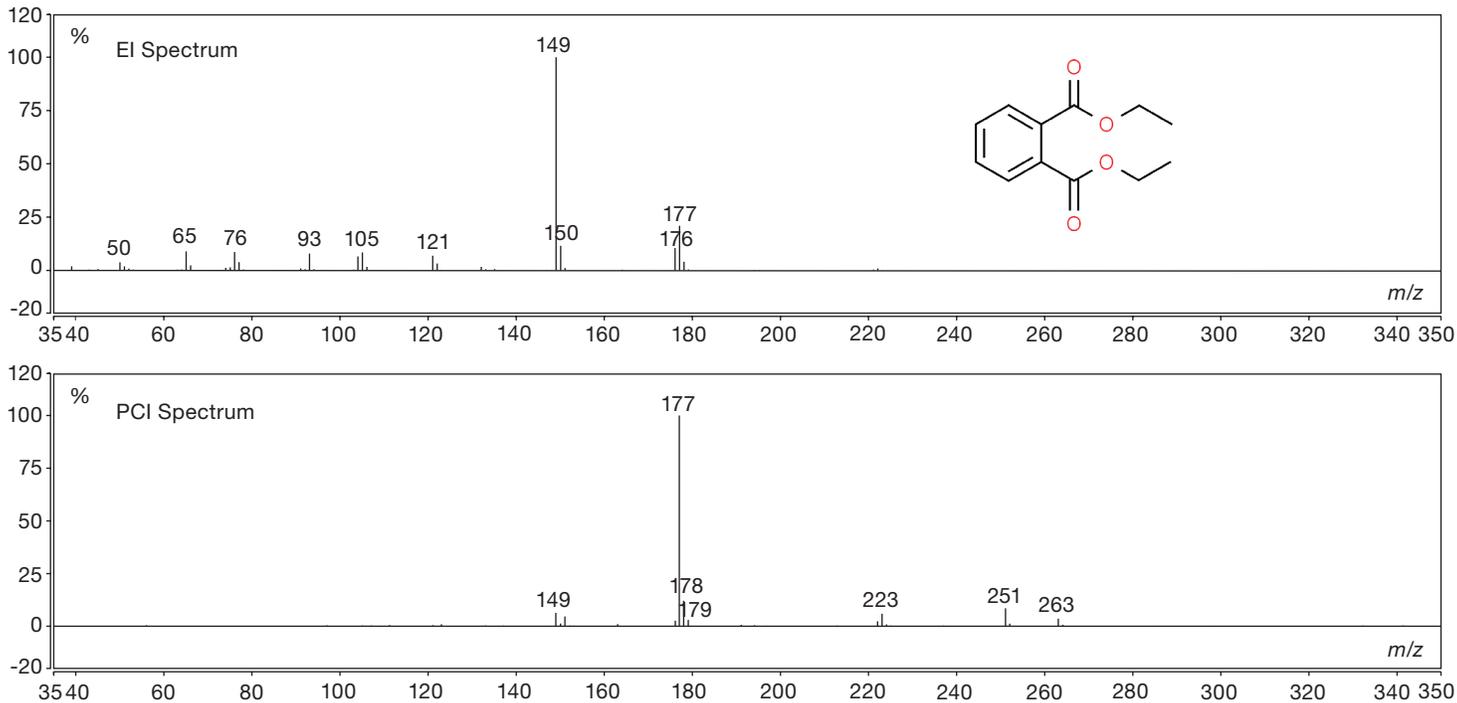Figure 6. Comparison of the mass spectrum for hexachlorocyclopentadiene in EI and PCI modes

Figure 7. Comparison of mass spectrum for diethylphthalate in EI and PCI modes

Effect of source temperature on positive chemical ionization

The ion source temperature has a pronounced effect on PCI mass spectral pattern of an analyte molecule. This can be exemplified by the mass spectral pattern for phenanthrene (molecular weight - 178 Da) at various ion source temperatures in Figure 8. The ion source temperature was varied from 150 ℃ to 320 ℃, and we can observe that adduct formation and protonation reduces with increasing temperature.
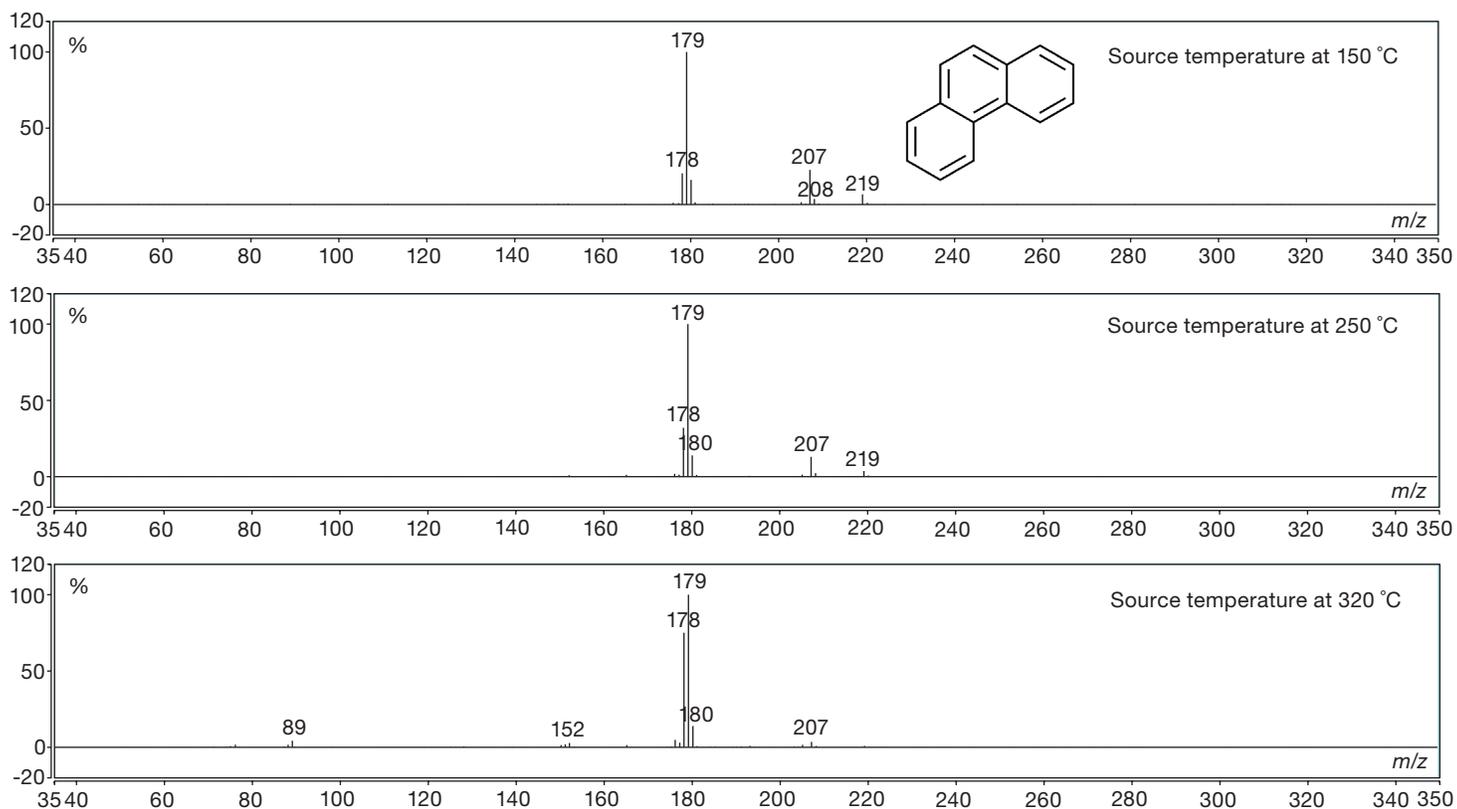

Figure 8. Effect of ion source temperature on fragmentation pattern

Thus, higher ion source temperatures are less useful for molecular weight confirmation of analytes. However, higher temperatures are recommended for keeping the source more robust as lower temperatures tend to foul the ion source rapidly with reagent gases such as methane and iso-butane. It is recommended to use a higher ion source temperature for quantitation purposes once the identity of the compound is confirmed. The ability to remove the source without venting the MS on the NeverVent system allows for easy ion source removal for cleaning purposes. NeverVent technology allows the rapid switching between dedicated ionization EI and CI ionization modes without breaking vacuum. This technology allows the instrument to be quickly purposed for the analysis of interest with minimal downtime.

Conclusion

The primary purpose of this technical note is to educate the reader on positive chemical ionization mode used in GC-MS analytical techniques and to show the performance on the ISQ 7610 system. The examples of the 8270 SVOC compounds and the comparison of the EI and methane-PCI spectra showed the advantages of using PCI for analyte confirmation. Low ion source temperature is best suited to determine an unknown analyte molecular weight, and higher temperatures are recommended for robustness and quantitation. The utilization of NeverVent technology on the ISQ 7610 GC-MS allows users to change between dedicated ionization modes, clean the ion source, and exchange the analytical column without breaking instrument vacuum. This technology minimizes instrument downtime and maximizes the number of samples that can be run on the system.

References

1. Sparkman, O. D.; Penton, Z. E.; Kitson, F. G. Gas Chromatography and Mass Spectrometry – A Practical Guide; Academic Press, 2011.
2. Harrison, A. G. Chemical Ionization Mass Spectrometry; CRC press, 1992.
3. Hübschmann, H-J. Handbook of GC-MS: Fundamentals and Applications; Wiley-VCH, 2015

Learn more at **thermofisher.com**

thermo scientific